ORGANIC THIN FILM ELECTROLUMINESCENCE (EL) ELEMENT

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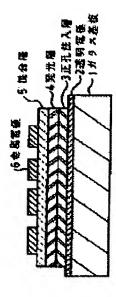
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Abstract of JP3274695

PURPOSE:To extend service life as well as enable high bright multicolor luminescence with a constant voltage by inserting a mixed layer including an electrode material and charged electrode implantation material, or an electrode material and organic fluorescent material, between one covering layer and an electrode. CONSTITUTION: After a transparent electrode 2 made of ITO and the like is formed on a glass base 1, a hole implantation layer 3 made of N,N',N'tetraphenyl-4,4'-ciaminobiphenyl is formed thereon, and then an EL layer 4 is formed thereon using tris(8hydroxyquinoline)aluminum as an organic fluorescent material. Then a mixed layer is formed thereon which layer includes organic charge moving complex made of TTF (tetrathiofurvalene) and TCNQ (tetracianoquinodimethane). Finally, a metal electrode 6 of alloy where Mg and In are mixed at the ratio of 10:1 is formed to complete an organic thin film EL element. It is thus possible to disperse the concentrated



homogeneous layer on an electrode interface, to extend the width of electric charge layer, and restrain rising of energy interference width. It is thus possible to provide high bright multicolor luminescence, improveclose contact with the electrode, and reduce degrading in an EL element.

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会発明の名称 有機薄膜EL素子

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明日間

1. 発明の名称

有機薄膜EL素子

- 2. 特許請求の範囲
- (1) 少なくとも一方が透明である一対の電極間に、 少なくとも1以上の電荷注入層と少なくとも1 以上の有機蛍光体よりなる発光層との積層膜が 形成された有機薄膜EL素子において、少なく とも一方の積層膜と電極との間に有機電荷移動 錯体と電荷注入材料あるいは有機電荷移動鉛体 と有機蛍光体を含む混合層を挿入したことを特 徴とする有機薄膜EL素子。
- (2) 少なくとも一方が透明である一対の電極間に、 少なくとも1以上の電荷注入層と少なくとも1 以上の有機蛍光体よりなる発光層との積層膜が 形成された有機薄膜EL素子において、少なく とも一方の積層膜と電極との間に電極材料と電 荷注入材料あるいは電極材料と有機蛍光体を含 む混合層を挿入したことを特徴とする有機薄膜

EL素子。

3. 発明の詳細な説明

[産業上の利用分野]

本発明は平面光源やディスプレイに使用される 有機薄膜発光素子に関するものである。

「従来の技術」

有機物質を原料としたEL(電界発光)素子は、 その豊富な材料数と分子レベルの合成技術で、安 価な大面積フィルム状フルカラー表示素子を実現 するものとして注目を集めている。例えばアント ラセンやペリレン等縮合多環芳香族系を原料とし てLB法や真空蒸巻法等で薄膜化した直流駆動の 有機薄膜発光素子が製造され、その発光特性が研究されている。

さらに、最近有機薄膜を2層構造にした新しいタイプの有機薄膜発光素子が報告され、強い関心を集めている(アプライド・フィジックス・レターズ、51巻、 913ページ、1987年)。報告によれば、第4図に示すように、強い蛍光を発する金属キレート化合物を発光層44に、アミン系材料を正

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孔伝導性有機物の正孔注入圏43に使用し、これらをガラス基板41上に形成された透明電極42と金属電極45との間に挿入することにより、明るい緑色発光を得たことが開示されており、6~7 Vの直流印加で約100 cd/n² の輝度を得ている。

この有機薄膜EL素子は、簡便な真空蒸着法と 100℃以下の低温成膜プロセスで製造でき、かつ 赤から育までの発光素子を安価に提供できる可能 性を秘めている。

[発明が解決しようとする課題]

りなる発光層との積磨膜が形成された有機薄膜 E し素子において、少なくとも一方の積層膜と電極 との間に電極材料と電荷注入材料あるいは電極材 料と有機蛍光体を含む混合層を挿入したことを特 徴とする有機薄膜 E し素子である。

[作用]

有機薄膜EL素子の印加電圧に対する発光特性が、電圧印加時間と共に高電圧側にシフトする現象は、有機薄膜EL素子に使用している有機材料に対する依存性は少なく、素子構造自体に原因がある。

 本発明は以上述べたような課題を克服して、定 電圧で多色・高輝度発光が可能であり、素子劣化 が少なく長寿命で実用性のある有機薄膜EL素子 を提供することを目的とする。

[課題を解決するための手段]

前述の課題解決のために本発明が提供する手段は、少なくとも一方が透明である一対の電極間に、少なくとも1以上の電荷注入層との積層膜が形成された有機薄膜EL素子において、少なくとも1方の積層膜と電極との間に有機電荷移動錯体と有機で含む混合層を挿入したことを特徴とする有機薄膜EL素子である。

本発明が提供する他の手段は、少なくとも一方 が透明である一対の電極間に、少なくとも1以上 の電荷注入層と少なくとも1以上の有機蛍光体よ

圧が電圧印加時間と共に上昇してゆく。

ホモ電荷層とエネルギー障壁の上昇の関係は、 界面に蓄積される電荷量と電荷層幅のべき乗に比 例している。電極と有機薄面に比較的抵抗 の低い層を挿入し、電極界面に集中していたホモ 電荷層を分散し、電荷層幅を広げることにより、 エネルギー障壁幅の上昇を抑えることができる。 本発明においては、ホモ電荷層の緩和・中和の 法として、電極と接する有機薄膜層に有機電荷移 動錯体あるいは電極材料を添加した混合層を挿入 する。

また、電極との界面に混合層を挿入することで、 電極との密着性が向上するので、その結果、電極 剥離による素子劣化を大幅に低減できる。

[実施例]

以下、本発明の実施例について詳細に説明する。 実施例1

第 1 図に示すように、ガラス基板1上にITOなどからなる透明電極2を形成してから、N.H.N',N'-テトラフェニル-4,4'-ジアミノビフェ

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ニル(以下、ジアミンと略記する。)からなる正孔注入層3を 600 Å、有機蛍光体としてトリス(8-ハイドロキシキノリン)アルミニウム(以下、アルミキノリンと略記する。)を使用して発光層4を 500 Å形成した。引き続いて、TTF(テトラチオフルバレン)とTCNQ(テトラシアノキノジメタン)からなる有機電荷移動錯体とアルキノジメタン)からなる有機電荷移動錯体とアルミキノリンを含む混合層 5 を第2図に示すような連続的に変化する分布で 300 Å形成する。最後にMgと『nを10:1で混合した合金の金属電極6を電子ビーム蒸着法で 1500 Å形成して有機薄膜発光素子が完成する。

この素子の発光特性を乾燥窒素中で測定したところ、約5 Vの直流電圧の印加で300 cd/m² の緑色の発光が得られた。この有機薄膜発光素子を電流密度 0.5 ma/cm² の状態でエージング試験をしたところ、輝度半減時間は 1000 時間以上であった。 世来の素子では 100から 500時間であったから、この素子の信頼性は大幅に改善されている。また、電気特性のシフトも5 V程度と、従来より

実施例2

第1図と同じ構造で、 610 nm から 630 nm に 強い蛍光を発するペリレン誘導体を発光層4に用 い、正孔注入層3としてトリフェニルメタン誘導 体を用いた有機薄膜EL素子を作製した。混合層 5はペリレン誘導体 100%からMg 100%まで、 電極方向に連続的に変化させた。最後にMgと 1 nが 10 : 1 で混合した合金の金属電極6を電 子ピーム蒸替法で 1500 人形成して有機薄膜発光 素子が完成する。

このようにして作製した有機薄膜EL素子は金属電極と有機発光層の密着性に優れ、長時間駆動しても電極の剥離は観測できなかった。 実施例3

第3図に示すように、530 nuから 550 nm に強い蛍光を発するナフタルイミド誘導体を発光層34に、電子注入層35としてアルミキノリンを用いた。混合層33および36はそれぞれナフタルイミド誘導体とCulx を、およびアルミキノリンとTTF・TCNQ錯体をそれぞれ連続的に変化したもの

大幅に低下した。

本実施例ではトリス(8-ハイドロキシキノリン) アルミニウム有機蛍光体を用いたが、アントラセ ン誘導体、ピレン誘導体、テトラセン誘導体、ス チルベン誘導体、ペリレン誘導体、キノン誘導体。 フェナンスレン誘導体、ナフタン誘導体、ナフタ ルイミド誘導体、フタロペリノン誘導体、シクロ ペンタジェン誘導体、シアニン誘導体、その他可 視領域で強い蛍光を発する有機物を発光層4の材 科に使用しても同様な効果が認められた。また、 これらの有機蛍光体に、10⁻⁵~10⁻² mol 程度のロ ーダミン、シアニン、ピラン、クマリン、フルオ レン. POPOP. PBBO等、他の蛍光の強 い有機分子をさらに添加して、発光波長を変える ことができる。透明電極2はITO以外に、Zn O: Al tSnO2: Sb. In2 O3 . Au. Cul_x、Ptなど仕事関数が 4.5 eV以上ある 導電性材料であればよい。

また金属電極6は透明電極2より仕事関数が低いものであればMgIn以外でもよい。

電子注入層35の材料としては、アントラセン、テトラセンなどを用いてもよい。更に、ジアミン等、正孔注入層を正孔注入電極であるITO界面に挿入した4層あるいはITO界面と正孔注入層の間に、例えばジアミンにCuIχ を添加した混合層を挿入した5層構造の素子でも同様な効果が得られた。

なお、本実施例では、いずれも混合圏として、 その組成が連続的に変化したものを用いたが、不 連続に変化するもの、あるいは均一組成のもので あってもよい。また、混合圏に含ませる材料は、 隣接する電極あるいは有機圏の構成成分に限定さ れることはなく、要求特性を満足するものであれ ばよい。

[発明の効果]

以上述べたように、本発明により従来の有機薄

膜EL素子に比べて発光特性の駆動時間に対する 特性のドリフトが少ない優れた素子を提供するこ とが可能となった。更に、電極の剥離による素子 劣化も減少し、長寿命の有機薄膜EL素子が提供 できる。

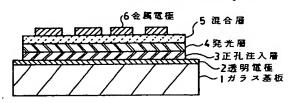
4. 図面の簡単な説明

第1図は本発明の一実施例の断面図、第2図は 第1図実施例における混合層の組成分布図、第3 図は本発明の別の一実施例の断面図、第4図は従 来技術による有機薄膜EL素子の断面図である。

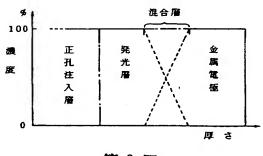
- 1,31.41…ガラス基板
- 2,32,42…透明電極
- 3. 43…正孔往入廳
- 4,34,44…発光層
- 5.33.36…混合磨
- 6,37,45…金属電極
- 35… 電子注入層

特許出願人 日本電気株式会社代理 人 弁理士 舘 野 千 惠 子

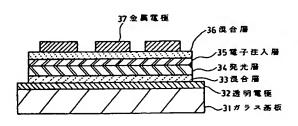
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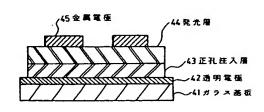
第1図



第 2 図



第 3 図



第 4 図

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Specification

1. Title of the Invention

ORGANIC THIN FILM EL ELEMENT

- 2. Scope of Claims
- (1) An organic thin film EL element comprising:
- a laminated film in which at least one electric charge implanting layer and at least one light emitting layer made of an organic fluorescent substance are formed between a pair of electrodes at least one of which is transparent, characterized in that a mixed layer including an organic electric charge transferring complex and an electric charge implanting material, or an organic electric charge transferring complex and an organic fluorescent substance is inserted between at least one laminated film and an electrode.
- (2) An organic thin film EL element comprising:
- a laminated film in which at least one electric charge implanting layer and at least one light emitting layer made of an organic fluorescent substance

are formed between a pair of electrodes at least one of which is transparent, characterized in that a mixed layer including an electrode material and an electric charge implanting material, or an electrode material and an organic fluorescent substance is inserted between at least one laminated film and an electrode.

3. Detailed Description of the Invention [Industrial Field of the Invention]

The present invention relates to an organic thin film light emitting element used for a plane light source or a display.

[Prior Art]

An EL (electroluminescence) element of which material is an organic substance receives much attention since it can realize a large area film shape full color display element at low cost due to an abundance of materials and a synthetic technology in molecular level. For example, a DC driven organic thin film light emitting element is manufactured to be a thin film by an LB method, a vacuum evaporation method or the like using condensation polycyclic aromatic series such as anthracene or perylene as a material and light emitting characteristics thereof are studied.

Furthermore, a new type of organic thin film light emitting element which has a two-layer structure of organic thin films has recently been reported and receives much attention (on page 913 of Applied Physics Letters vol. 51 in 1987). According to the report, as shown in Fig. 4, it is disclosed that a light emitting layer 44 made of a metal chelate compound which emits strong fluorescence and a hole implanting layer 43 of a hole conductive organic substance which uses an amine-based material are inserted between a transparent electrode 42 formed over a glass substrate 41 and a metal electrode 45, so that bright green light emission can be obtained, and a luminance of approximately 100 cd/m² is obtained by DC application of 6 to 7V.

This organic thin film EL element can be manufactured by a simple vacuum evaporation method and a low temperature film formation process of 100°C or less, and has the possibility of providing red to blue light emitting elements at a low cost.

[Problems to be Solved by the Invention]

However, light emitting characteristics relative to an application voltage of an organic thin film EL element having the structure shown in Fig. 4 tend

to shift to a high voltage side with a voltage application time, and this phenomenon is observed even if an organic material is substituted, which is considered to be caused by the structure of the element itself. Such a phenomenon that the light emitting characteristics are varied as the element is driven causes the following problems. That is, a rise of a light emitting threshold voltage makes it difficult to perform the constant voltage driving which is an easy driving method, furthermore causes deterioration of the light emitting efficiency. Besides, a rise of a driving voltage to compensate the luminance deterioration causes acceleration of the element deterioration due to the element light emitting efficiency, dielectric breakdown and heat release.

It is an object of the present invention to solve the aforementioned problems and provide a practical organic thin film EL element which enables light emission with full color and high luminance at a constant voltage and has a long lifetime with less element deterioration.

[Means for Solving the Problems]

A means provided by the present invention to solve the above problems is an organic thin film EL element comprising a laminated film in which at least one electric charge implanting layer and at least one light emitting layer made of an organic fluorescent substance are formed between a pair of electrodes at least one of which is transparent, characterized in that a mixed layer including an organic electric charge transferring complex and an electric charge implanting material, or an organic electric charge transferring complex and an organic fluorescent substance is inserted between at least one laminated film and an electrode.

Another means provided by the present invention is an organic thin film EL element comprising a laminated film in which at least one electric charge implanting layer and at least one light emitting layer made of an organic fluorescent substance are formed between a pair of electrodes at least one of which is transparent, characterized in that a mixed layer including an electrode material and an electric charge implanting material, or an electrode material and an organic fluorescent substance is inserted between at least one laminated film and an electrode.

[Action]

A phenomenon that light emitting characteristics relative to an application voltage of an organic thin film EL element shift to a high voltage side with a voltage application time is independent of an organic material

which is used for the organic thin film EL element, and is caused by the structure of the element itself.

That is, the light emitting characteristics shift to the high voltage side since the energy barrier on an electrode interface increases with the voltage application time. This point has been carefully studied, and it is proved that a deep trap level is generated on the electrode interface by implanting strong electric field electric charges and thus the same polarity electric charge layer, namely a homo electric charge layer is formed on the electrode interface. The newly formed homo electric charge layer increases the energy barrier on the interface. Homo electric charges are stored with the element driving, as a result, a driving voltage rises with the voltage application time.

The relation between the homo electric charge layer and the rise of the energy barrier is in proportion to the power of the quantity of electric charges which are stored on the interface and the width of the electric charge layer. It is possible to restrain the rise of the width of the energy barrier by inserting a layer having a relatively low resistance between an electrode and an organic thin film, by dispersing the homo electric charge layer which is condensed on the electrode interface, and by increasing the width of the electric charge layer. In the present invention, as a method of relaxation and neutralization of the homo electric charge layer, a mixed layer in which an organic electric charge transferring complex or an electrode material is added to an organic thin film layer in contact with an electrode is inserted.

Besides, adhesive properties with the electrode is improved by inserting the mixed layer onto the interface with the electrode, as a result, the element deterioration due to the electrode peeling can be reduced significantly.

[Embodiment]

Hereinafter, an embodiment of the present invention is described in detail.

Embodiment 1

As shown in Fig. 1, after a transparent electrode 2 made of ITO or the like is formed on a glass substrate 1, a hole implanting layer 3 made of N, N, N', N'-tetraphenyl-4, 4'-diaminobiphenyl (hereinafter referred to as diamine) is formed to have a thickness of 600 Å, and a light emitting layer 4 is formed to have a thickness of 500 Å by using tris(8-hydroxyquinoline)aluminum (hereinafter referred to as alumiquinoline) as an organic fluorescent substance. After that, a mixed layer 5 containing an organic electric charge transferring

complex made of TTF (tetrathiofulvalene) and TCNQ (tetracyanoquinodimethane) and alumiquinoline is formed to have a thickness of 300 Å having a distribution which is varied continuously as shown in Fig. 2. Finally, a metal electrode 6 made of an alloy in which Mg and In are mixed in a ratio of 10: 1 is formed to have a thickness of 1500 Å by electron beam evaporation, so that an organic thin film light emitting element is completed.

When the light emitting characteristics of this element are measured in an atmosphere of dry nitrogen, green light emission of 300 cd/m² is obtained by applying a direct voltage of approximately 5 V. When an aging test is performed on this organic thin film light emitting element under the condition of a current density of 0.5 mA/cm², time when the luminance is reduced to half is 1000 hours or more. In the case of a conventional element, it is 100 to 500 hours; therefore, the reliability of this element is improved substantially. In addition, a shift of the electric characteristics is about 5 V, which is reduced significantly compared with the conventional one.

Tirs(8-hydroxyquinoline)aluminum organic fluorescent substance is used in the present embodiment, however, the same effect can be obtained when an organic substance which emits strong fluorescence in a visible field is used as a material for the light emitting layer 4 such as anthracene derivative, pyrene derivative, tetracene derivative, stilbene derivative, perylene derivative, quinone derivative, phenanthrene derivative, naphthane derivative, derivative. naphthalimido phthaloperinone derivative, cyclopentadiene derivative or cyanine derivative. Furthermore, a light emitting wavelength can be varied by further doping these organic fluorescent substance with other strong fluorescent organic molecular such as rhodamine, cyanine, pyran, coumarin, fluorene, POPOP or PBBO of approximately 10⁻⁵ to 10^{-2} mol. In addition to ITO, a conductive material having a work function of 4.5 eV or more such as ZnO:Al, SnO₂:Sb, In₂O₃, Au, CuI_x or Pt can be used for the transparent electrode 2.

Furthermore, the metal electrode 6 can be formed of another material besides MgIn, if the work function is lower than that of the transparent electrode 2.

Embodiment 2

An organic thin film EL element where a perylene derivative which emits strong fluorescence from 610 nm to 630 nm is used for the light emitting layer 4 and a triphenylmethane derivative is used for the hole

implanting layer 3 is formed using the same structure as that of Fig. 1. The mixed layer 5 is varied continuously in the direction of an electrode from perylene derivative 100% to Mg 100%. Finally, the metal electrode 6 made of an alloy in which Mg and In are mixed in a ratio 10: 1 is formed to have a thickness of 1500 Å by the electron beam evaporation, so that an organic thin film light emitting element is completed.

The organic thin film EL element formed in this way is excellent in adhesive properties between the metal electrode and the organic light emitting layer, and peeling of the electrode is not observed even when the element is driven for a long time.

Embodiment 3

A naphthalimido derivative which emits strong fluorescence from 530 nm to 550 nm is used for a light emitting layer 34 and alumiquinoline is used for an electron implanting layer 35 as shown in Fig. 3. Mixed layers 33 and 36 are formed by continuously varying a naphthalimido derivative and CuI_x, and alumiquinoline and TTF•TCNQ complex respectively. Finally, a back metal electrode 37 made of an alloy in which Mg and In are mixed in a ratio 10: 1 is formed to have a thickness of 1500 Å by the electron beam evaporation, so that an organic thin film light emitting element is completed.

As a material for the electron implanting layer 35, it is possible to use anthracene, tetracene and the like. Furthermore, the same effect can be obtained using an element having a four-layer structure where a hole implanting layer such as diamine is inserted onto an ITO interface that is a hole implanting electrode, or a five-layer structure where a mixed layer containing diamine doped with CuI_x for instance is inserted between the ITO interface and the hole implanting layer.

In addition, the mixed layer of which composition is varied continuously is used in all the embodiments, however, it is possible to use the mixed layer of which composition is varied discontinuously or is uniform. Moreover, a material contained in the mixed layer is not limited to a component of an adjacent electrode or organic layer, and may be any material as long as it satisfies the required characteristics.

[Effects of the invention]

As stated above, the present invention allows to provide an excellent element having less drift of light emitting characteristics relative to a driving time compared with the conventional organic thin film EL element. Furthermore, the element deterioration due to peeling of an electrode is reduced and the organic thin film EL element with a long lifetime can be provided.

4. Brief Description of the Drawings

Fig. 1 shows the cross section of one embodiment of the present invention; Fig. 2 shows a component distribution of a mixed layer in an embodiment of Fig. 1; Fig. 3 shows the cross section of another embodiment of the present invention; and Fig. 4 shows the cross section of an organic thin film EL element by the conventional technology.

1, 31, 41 ... glass substrate

2, 32, 42 ... transparent electrode

3, 43 ... hole implanting layer

4, 34, 44 ... light emitting layer

5, 33, 36 ... mixed layer

6, 37, 45 ... metal electrode

35 ... electron implanting layer

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